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Procédé de polymérisation

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Description

[0001] The present invention relates to a process for preparing copolymers, in particular to a process for preparing copolymers of ethylene with alpha-olefins having a bimodal molecular weight distribution.

[0002] Bimodal or multimodal polyolefins with broad molecular weight distributions are obtained commercially using Ziegler catalysts in slurry or gas phase polymerisation processes in which different operating conditions are employed. Such processes are known as cascade processes. Polymers obtained in such processes often selectively incorporate comonomers in one part of the molecular weight distribution. Other parts of the polymer often contain little or no comonomer incorporation.

[0003] These polymers have been found to offer advantages in processability and tear, impact, stress crack and fracture properties depending upon the polymer application envisaged.

[0004] The cascade process relies upon different operating conditions, often using two separate reactors. It would be advantageous to be able to produce such polymers in a single reactor preferably in the gas phase under steady state conditions.

[0005] Bimodal polyolefins may be prepared by using combinations of polymerisation catalysts as components, for example a metallocene and a Ziegler catalyst or alternatively two different metallocene catalysts may be used. Such catalyst systems may be referred to as multisite catalysts. In such systems the different catalyst components must be able to produce polyolefins of different molecular weights under a single set of reactor process operating conditions, so that a bimodal molecular weight distribution is formed. Typically the low molecular weight portion of such bimodal polymers are derived from the metallocene component(s) of the catalyst.

[0006] It would also be desirable to use multisite catalysts to prepare polyolefins with specific comononer distributions across their bimodal molecular weight distributions. Unfortunately metallocene components conventionally used in multisite catalysts are known for the ability to incorporate high quantities of comonomer relative to Ziegler catalysts, resulting in bimodal MWD polymers in which comonomer is concentrated in the low MW portion.

[0007] For example EP 586168 discloses metallocene complexes in which the complex comprises cyclopentadienyl ligands having single alkenyl group substitutents. In this disclosure the complexes are used with other polymerisation catalysts to form multisite catalysts.

[0008] It has now been found that certain metallocene components having a multitude of substitution on the ligands have a low propensity for incorporating comonomer into bimodal polymer even in the presence of high concentrations of comonomer and may be utilized to control the comonomer distribution.

[0009] The comonomer distribution is dependent upon the comonomer incorporation properties of the individual components of the multisite catalyst. Hence by using such metallocene components having a low propensity for incorporating comonomer, polymers may be obtained which typically exhibit a bimodal comonomer distribution in which the comonomer is more evenly distributed over the MWD or is even concentrated in the high molecular weight component.

[0010] Thus according to the present invention there is provided a process for preparing bimodal molecular weight distribution copolymers of ethylene with alpha-olefins having 3 to 20 carbon atoms, said copolymers having:- (a) a comonomer distribution wherein the comonomer level at the mid-position of the low molecular weight component is <3 times the level at the mid position of the high molecular weight component, and (b) a total average comonomer content in the range 0.5-20 short chain branches (SCB)/1000 C atoms wherein said process comprises polymerizing ethylene with alpha olefins in the presence of a supported multisite catalyst, said catalyst comprising a Ziegler catalyst component and a metallocene component having any of the formulae:

$$\text{(I)} \qquad (C_5R_5)\,(C_5R^1{}_5)MY_2$$

$$\text{(II)} \qquad (C_5R_2H_3)(C_5R^1{}_2H_3)MY_2$$

$$\text{(III)} \qquad (C_5R_4)Z(C_5R^1{}_4)MY_2$$

$$\text{(IV)} \qquad (C_5R_mH_{5-m})(C_5R^1{}_nH_{5-n})MY_2$$

wherein,

C_5R_5 and $C_5R^1{}_5$ etc represent a cyclopentadienyl ligand,
R and R^1 are alkyl, aryl, alkylaryl, alkenyl, or haloalkyl groups and may be the same or different,

Z is bridging group
M is Zr, Ti or Hf.
Y is a univalent anionic ligand

and wherein in Formula (II) at least one of R and R^1 has ≥ 3 carbon atoms and in Formula (IV) m 3 or 4 and n is 5 or less.

[0011] The "comonomer level" defined in (a) represents the comonomer content, measured in short chain branches per thousand backbone carbon atoms (SCB/1000C), of the polymer at the specified molecular weight which is independent of the proportion of the total polymer represented by the polymer at that molecular weight.

[0012] The "total average comonomer content" defined in (b) is the average comonomer content, in SCB/1000C, of all polymer over the entire molecular weight range.

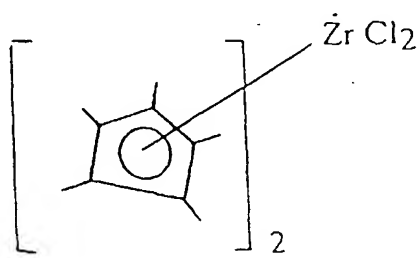
[0013] The multisite catalyst is defined as comprising two active components for example a Ziegler catalyst component producing a high molecular weight polymer component and a metallocene component producing a low molecular weight polymer component. The metallocene component may also be comprised of two or more different metallocene species provided that together they provide the required low molecular weight polymer component.

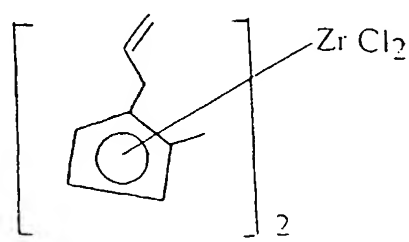
[0014] Metallocenes suitable for use in the present invention are those wherein:

Z = bridging group comprising CX_2, SiX_2, GeX_2 etc., and
Y= univalent anionic ligand for example halide, alkyl, alkoxy, etc.

[0015] Examples of suitable metallocenes as represented by Formula (I) and (II) are bis(pentamethylcyclopentadienyl) zirconium dichloride and bis(1-propenyl-2-methylcyclopentadienyl) zirconium dichloride respectively.

[0016] These metallocenes are represented by the Formula:





[0017] By using the multisite catalysts of the present invention, polymer compositions containing a lower absolute comonomer incorporation level may be obtained for a given set of reaction conditions.

[0018] The metallocenes may be prepared in accordance with literature methods eg J E Bercaw et al JACS 100, 10, 3078, Canadian Journal of Chemistry 69, 1991, 661-672 and E Samuel et al J. Organometallic Chem. 1976, 113, 331-339.

[0019] Bimodal distribution is defined as relating to copolymers which show a substantially different molecular weight distribution between the low and the high molecular weight components.

[0020] Typically the low molecular weight component has a mid-position in the range 1000-300,000 preferably in the range 5000-50,000 and the high molecular weight component has a mid-position in the range 100,000 - 10,000,000 preferably in the range 150,000 - 750,000.

[0021] The total average comonomer content is preferably in the range 1 to 20 SCB/1000 C atoms.

[0022] The multisite catalyst for use in the present invention may be used in the presence of suitable co-catalysts. Suitable co-catalysts are organometallic compounds having a metal of Group 1A, IIA, IIB or IIIB of the periodic table. Preferably, the metals are selected from the group including lithium, aluminium, magnesium, zinc and boron. Such co-catalysts are known for their use in polymerisation reactions, especially the polymerisation of olefins, and include organo aluminium compounds such as trialkyl, alkyl hydrido, alkyl halo, alkyl alkoxy aluminium compounds and alkyl aluminoxanes. Suitably each alkyl or alkoxy group contains 1 to 6 carbons. Examples of such compounds include trimethyl aluminium, triethyl aluminium, diethyl aluminium hydride, triisobutyl aluminium, tridecyl aluminium, tridodecyl aluminium, diethyl aluminium methoxide; diethyl aluminium ethoxide, diethyl aluminium phenoxide, diethyl aluminium chloride, ethyl aluminium dichloride, methyl diethyoxy aluminium and methyl aluminoxane.

[0023] The preferred compounds are alkyl aluminoxanes, the alkyl group having 1 to 10 carbon atoms, especially methyl aluminoxane (MAO) and trialkyl aluminium compounds eg trimethylaluminium. Other suitable co-catalysts also

include Bronsted or Lewis acids.

[0024] The co-catalyst may be mixed with the supported multisite catalyst. For example the metallocene component and co-catalyst (eg MAO) may be added to a supported Ziegler catalyst. During the subsequent polymerisation process a second cocatalyst (eg trimethylaluminium) may be added to the reaction medium.

[0025] Catalyst supports used with the multisite catalyst may comprise a single oxide or a combination of oxides or metal halides. They may also be physical mixtures of oxides or halides. The supports may have a high surface area (250-1000M^2/g) and a low pore volume (0-1ml/g) or a low surface area (0-250M^2/g) and high pore volume (1-5ml/g) or preferably high surface area (250-1000M^2/g) and high pore volume (1-5ml/g) (mesoporous). Preferred support materials are silica, alumina, titania, boria and anhydrous magnesium chloride or mixtures thereof, although any support used in heterogeneous catalysis/polymer catalysis may be employed.

[0026] The support may undergo a pretreatment to modify its surface eg thermal or chemical dehydroxylation or any combination of these, using agents such as hexamethyldisilazane and trimethylaluminium. Other reagents that can be used are triethyaluminium, methylaluminoxane and other aluminium containing alkyls, magnesium alkyls especially dibutyl magnesium and alkyl magnesium halides, zinc alkyls and lithium alkyls. Different impregnation regimes may be used to add the surface treatment and subsequent catalyst impregnation. Impregnation may take place sequentially or in a number of separate steps or in a single step using any method known in the prior art including vapour phase treatment/impregnation techniques.

[0027] The component of the multisite catalyst which provides the high molecular weight component may suitably be a conventional Ziegler catalyst, a Phillips catalyst or alternatively another metallocene catalyst. Preferably the high molecular weight component is a Ziegler catalyst.

[0028] A suitable catalyst is disclosed in European Application No. EP 595574.

[0029] The multisite catalyst used in the process according to the present invention may be used to produce polymers using solution polymerisation, slurry polymerisation or gas phase polymerisation techniques. Suitably alpha olefins used in the copolymerisation may be butene-1, hexene-1, 4-methyl pentene-1 octene-1 or higher α -olefins which may be provided in-situ. Methods and apparatus for effecting such polymerisation reactions are well known and described in, for example, Encyclopaedia of Polymer Science and Engineering published by John Wiley and Sons, 1987, Volume 7, pages 480 to 488 and 1988, Volume 12, pages 504 to 541. The multisite catalyst composition according to the present invention may be used in similar amounts and under similar conditions to known olefin polymerisation catalysts.

[0030] The polymerisation may optionally be carried out in the presence of hydrogen. Hydrogen or other suitable chain transfer agents may be employed in the polymerisation to control the molecular weight of the produced polyolefin. The amount of hydrogen may be such that the ratio of the partial pressure of hydrogen to that of olefin(s) is from 0.0001-1, preferably 0.001-0.1.

[0031] Typically, the temperature is from 30 to 110°C for the slurry or "particle form" process or for the gas phase process. For the solution process the temperature is typically from 100 to 250°C. The pressure used can be selected from a relatively wide range of suitable pressure, eg from sub-atmospheric to about 350 MPa. suitably, the pressure is from atmospheric to about 6.9 MPa, or may be from 0.05-10, especially 0.14 to 5.5 MPa. In the slurry or particle form process the process is suitably performed with a liquid inert diluent such as a saturated aliphatic hydrocarbon. Suitably the hydrocarbon is a C4 to C10 hydrocarbon, eg isobutane or an aromatic hydrocarbon liquid such as benzene, toluene or xylene. The polymer is recovered directly from the gas phase process, by filtration or evaporation from the slurry process and by evaporation from the solution process.

[0032] The process according to the present invention is particularly suitable for use in the gas phase.

[0033] By using the multisite catalysts of the present invention copolymer compositions containing a lower absolute comonomer incorporation level than comparable compositions when prepared under the same polymerisation reaction conditions may be prepared. This can lead to enhanced product properties for example higher stiffness for high density tough film. The ability to operate in the presence of a relatively high comonomer concentration yet produce products containing a low absolute comonomer level is also advantageous because it allows access to a wider range of molecular weight distribution for a given density range.

[0034] The present invention will now be illustrated with reference to the following examples.

Example 1

Preparation of Bis(propenylcyclopentadienyl)zirconium Dichloride (Comparative)

[0035] Allyl bromide (50g) was dissolved in tetrahydrofuran (200ml, dried) and cooled to 0°C. To this was added a tetrahydrofuran solution of sodium cyclopentadienylide (220ml, 2.0M) and the solution stirred for 16h. To the mixture was added saturated aqueous ammonium chloride solution (200ml); the organic phase was separated, washed with water (3 times with 200ml) and dried over anhydrous magnesium sulphate. The solution was filtered, the solvent removed on a rotary evaporator and the resulting yellow oil vacuum distilled (30-40°C, 17mmHg) to yield propenylcy-

clopentadiene (13.99g, 32.5% yield).

[0036] Methyl lithium solution (75.25ml, 1.4M in diethyl ether) was slowly added to a rapidly stirred solution of propenylcyclopentadiene (11.17g) in dry diethyl ether at 0°C. The reaction was warmed to 20°C and stirring continued until gas evolution had ceased. The precipitated lithium propenylcyclopentadienylide was isolated by filtration, washed with diethyl ether (2 times 100ml) and pumped to dryness to give 10.65g of fine white powder. To a rapidly stirred tetrahydrofuran solution (100ml) of the lithium propenylcyclopentadienylide at 0°C was added zirconium tetrachloride (11.09g, 47.5mmol) dissolved in dry tetrahydrofuran (100ml). The reaction mixture was allowed to warm to 20°C and was stirred for 16h. The volatiles were removed under vacuum, the residue extracted with diethyl ether (4 times 100ml) and filtered. The product was obtained as a microcrystalline white solid upon slow cooling of the solution to -78°C. Recrystallisation from cold ether yielded bis(propenylcyclopentadienyl)zirconium dichloride (13.33g, 75.4% yield).

Example 2

Preparation of Bis(1-propenyl-2-methylcyclopentadienyl)zirconium Dichloride

[0037] Propenylcyclopentadiene (7.5g) as prepared in Example 1 was dissolved in diethyl ether (100ml, dried) and cooled to -78°C. A diethyl ether solution of methyl lithium (55ml, 1.4M) was cautiously added, the cold bath was removed and the solution left stirring for 16h at 20°C. The solid lithium propenylcyclopentadienylide salt obtained was filtered, washed with cold diethyl ether (twice at 0°C, 50ml) and pumped to dryness (7.8g, 100% yield). The lithium salt was dissolved in tetrahydrofuran (100ml), cooled to -78°C, and to it was slowly added a tetrahydrofuran solution of methyl iodide (10g). The reaction was stirred for 16hrs at 20°C and then quenched with saturated aqueous ammonium chloride solution (200ml). Diethyl ether (50ml) was added, the organic phase isolated and washed with water (3 times 100ml). After drying over anhydrous magnesium sulphate the solution was filtered and the solvent removed under vacuum (18mmHg, 20°C) to yield a brown oil, shown by NMR to be methylpropenylcyclopentadiene with traces of solvent (7.4g yield).

[0038] Methylpropenylcyclopentadiene as prepared above (4.07g) was dissolved in diethyl ether (100ml, dried) and cooled to -78°C. A diethyl ether solution of methyl lithium (25ml, 1.4M) was cautiously added and the solution stirred at 20°C for 16hrs. The thick suspension obtained was pumped to dryness to yield an off-white powder of lithium methylpropenylcyclopentadienylide (4.17g, 97.5% yield) which was dissolved in tetrahydrofuran and cooled to 0°C. A slurry of $ZrCl_4$.2 tetrahydrofuran (5.0g) in tetrahydrofuran was added to the lithium salt solution and was stirred at 20°C for 72 hrs. The reaction was then quenched with dry hydrogen chloride gas at 0°C, pumped to dryness and the product extracted with dichloromethane (2 times 50ml). The volume of dichloromethane was reduced to 25ml and heptane was added until precipitation started. Precipitation was completed by cooling the solution to -20°C for 16h and the solid product bis(1-propenyl-2-methylcyclopentadienyl)zirconium dichloride was isolated by filtration, washed with hexane (2 times 50ml) and pumped dry. (2.7g, 52% yield).

Example 3

Bis-(pentamethylcyclopentadienyl)zirconium Dichloride

[0039] Bis-(pentamethylcyclopentadienyl)zirconium dichloride was purchased from Strem Chemicals (Fluorochem) and used as received.

Supported Ziegler Catalysts

Example 4

[0040] Silica (Crosfield ES70, dried at 800oC for 5h in flowing nitrogen, 20 kg) was slurried in hexane (110L, dry) and hexamethyldisilazane (Fluka, 30 mols, 0.8mM/g of silica) added with stirring at 50°C. 120L of hexane was added with stirring, the solid was allowed to settle, supernatant liquid removed by decantation and hexane (130L, dry) added with stirring. This hexane washing was repeated a further 3 times. Dibutylmagnesium (FMC, 30 mols, 1.5mM/g of silica) was added and stirred for 1h at 50°C. t-Butyl chloride (Hüls, 60 mols, 3mM/g of silica) was added and stirred for 1h at 50°C. To this slurry was added an equimolar mixture of titanium tetrachloride (Thann & Mulhouse, 3 mols, 0.15mM/g of silica) and titanium tetra-n-propoxide (Thann & Mulhouse, 3 mols, 0.15mM/g of silica) with stirring at 50°C for 2 hrs, followed by 5 washings with 130L hexane. The slurry was dried under a flowing nitrogen stream to give a solid, silica-supported Ziegler catalyst.

Example 5

[0041] Silica (Crosfield ES70, dried at 800°C for 5h in flowing nitrogen, 20 kg) was slurried in hexane (110L dry) and hexamethyldisilazane (Fluka, 30 mols, 1.5mM/g of silica) added with stirring at 5°C. The solid was allowed to settle, supernatant liquid removed by decantation and hexane (130L dry) added with stirring. This hexane washing was repeated a further 3 times. Dibutylmagnesium (FMC 30 mols, 1.5mM/g of silica) was added and stirred for 1h at 50°C. t-Butyl chloride (Hüls, 60 mols, 3mM/g of silica) was added and stirred for lh at 50°C. To this slurry was added an equimolar mixture of titanium tetrachloride (Thann & Mulhouse, 3 mols, 0.15mM/g of silica) and titanium tetra-n-propoxide (Thann & Mulhouse, 30 mols, 0.15mM/g of silica) with stirring at 50°C for 2 hrs at 80°C followed by 3 washings with 130L hexane. The slurry was dried under a flowing nitrogen stream to give a solid, silica-supported Ziegler catalyst.

Example 6

[0042] Silica (Crosfield ES70, dried at 800°C for 5h in flowing nitrogen, 14.8g) was slurried in hexane (150ml, dry) and hexamethyldisilazane (Fluka, 4.4mM, 1.5mM/g of silica) added with stirring at 80°C. The solid was allowed to settle, supernatant liquid removed by decantation and hexane (500ml, dry) added with stirring. This hexane washing was repeated a further 4 times. Dibutylmagnesium (FMC, 22.2mM, 1.5mM/g of silica) was added and stirred for 1h at 50°C. t-Butyl chloride (Hüls, 44.4mM, 3mM/g of silica) was added and stirred for 1h at 50°C. To this slurry was added titanium tetrachloride (Thann & Mulhouse, 11.1 mM 0.5mM/g of silica) with stirring at 50°C. The slurry was dried under a flowing nitrogen stream to give a solid, silica-supported Ziegler catalyst.

Multisite Catalysts

[0043] All operations were carried out under an atmosphere of dry nitrogen.

Example 7

(Comparative)

[0044] Bis-(propenylcyclopentadienyl)zirconium dichloride (0.0454g) was dissolved in a toluene solution of methylaluminoxane (Schering, 6.9ml of 2.65M solution) at 20°C with stirring. This was added to a silica-supported Ziegler catalyst (from Example 5, 2.5g) and the resulting thick slurry stirred for 75min at 20°C. The solvent was then removed at 20°C under vacuum to give a free-flowing powder.

Example 8

[0045] Bis-(1-propenyl-2-methylcyclopentadienyl)zirconium dichloride (0.0488g) was dissolved in a toluene solution of methylaluminoxane (Schering, 7.8ml of 2.35M solution), with a further 9.2ml toluene added. This was added to a silica-supported Ziegler catalyst (from Example 5, 2.5g) and the resulting thick slurry stirred for 180min at 50°C. The solvent was then removed at 20°C under vacuum to give a free-flowing powder.

Example 9

[0046] Bis-(1-propenyl-2-methylcyclopentadienyl)zirconium dichloride (0.039g) was dissolved in a toluene solution of methylaluminoxane (Schering, 6.3ml of 2.33M solution), with a further 7.7ml toluene added. This was added to a silica-supported Ziegler catalyst (from Example 6, 2g) and the resulting thick slurry stirred for 180min at 50°C. The solvent was then removed at 20°C under vacuum to give a free-flowing powder.

Example 10

[0047] Bis-(pentamethylcyclopentadienyl)zirconium dichloride (0.054g) was dissolved in a toluene solution of methylaluminoxane (Schering, 8ml of 2.35M solution), with a further 8ml toluene added, at 20°C with stirring. This was added to a silica-supported Ziegler catalyst (from Example 4, 2.5g) and the resulting thick slurry stirred for 75min at 50°C. The solvent was then removed at 20°C under vacuum to give a free-flowing powder.

Polymerisation Reactions

Example 11

(Comparative)

[0048] A 3 litre reactor equipped with helical stirrer was heated to 80°C for 1h under flowing nitrogen. Dry sodium chloride (300g) was then added with trimethylaluminium (TMA) solution (2 ml of 2 M TMA in hexanes) and the reactor heated to 80°C for 1h. The reactor was purged with nitrogen, cooled to 45°C and TMA solution (1.8 ml of 0.5M TMA in hexanes) added. The temperature was raised to 75°C and hydrogen (0.041 Kg/cm2) and 1-hexene (2 ml) added prior to addition of ethylene (8.06 Kg/cm^2). Reaction was started by injection of the catalyst of Example 7 (0.129g) into the reactor. The temperature was maintained at 75°C and ethylene added to maintain constant pressure. The gas phase was monitored by mass spectrometer and hydrogen and 1-hexene were added as necessary to maintain constant gas phase concentrations. After the designated polymerisation time (129 minutes) the reaction was quenched by rapid reduction of the reactor to atmospheric pressure purging with nitrogen and cooling to room temperature. Results are given in the accompanying Table 1.

Examples 12-14

[0049] The same procedure was carried out as described in Example 11 using the catalysts of Examples 8-10. Details are given below in the Table 1.

Analytical Methods

GPC-IR

[0050] An infrared flow-through cell, (pathlength 1mm) was used, coupled directly to the GPC columns in a Waters 150CV chromatograph. The tubing connecting the 150CV to the infrared cell was heated to 140°C. Samples were prepared as 0.5%(w/v) solutions in trichlorobenzene/80ppm ionol, heated to 140°C for two hours, to 160°C for two hours and then filtered through a stainless steel cup filter (0.5 microns). The sample solutions were characterised at 140°C using Shodex 10^{7}Å, 10^{4}Å, linear columns with an eluant flowrate of 1ml/minute, calibrated with narrow polystyrene standards of known molecular weight. A Bio-Rad FTS-60A FTIR spectrometer with Bio-Rad WIN-IR software was used to aquire the Infrared spectra, using a liquid nitrogen-cooled MCT detector, over the range 3010 to 2820 cm^{-1}, at a resolution of 4cm^{-1}. Typically, acquisition times were 30 secs (64 scans), and spectral acquisition carried out at 1 minute intervals. The background spectrum used was a solvent spectrum acquired during the period between sample injection and the first appearance of polyethylene. 500 scans were acquired for each background.

[0051] Branching levels were based on the ratio of the methyl band at 2958cm^{-1} to that of the methylene peak at 2927cm^{-1}. A linear baseline was constructed between 2990 and 2825cm^{-1}. Results were converted from peak ratios to branching levels using a conversion calculated from analysis of a polyethylene for which NMR branching data were known. Corrections were made for the contribution of the methylene peak at the frequency used for measuring methyl groups, calculated from a linear homopolymer. Corrections were also made for the contribution from methyl groups at chain ends, based on the molecular weight of the polymer as indicated by the GPC elution time. For the purposes of this measurement it was assumed that all methyl groups occur at the same frequency and that all have the same extinction coefficient. Molecular weights for polyethylenes were derived from polystyrene elution times using the Mark-Houwink relationship, and end corrections were based on the elution time halfway through each spectral acquisition, to correct for any change in composition during the acquisition of a spectrum.

[0052] The results of the analytical methods are given below in Table 2.

[0053] From Table 2 it can be clearly seen that the comonomer distribution in examples 12-14, as determined from the relationship between the comonomer level at the mid-positions of the low and high MW components is <3 whereas in example 11 (comparative) this value is >3 ie 4.2.

TABLE 1

Example	Catalyst Example	C2 Pressure (kg/cm^2)	H2 Pressure (kg/cm^2)	1-Hexene (ml)	Run Time (min)	Polymer Yield (g)	Activity (gPE/mmol(Ti+Zr).h.b.)
11	7	8.06	0.041	2	129	193	372
12	8	8.16	0.061	1.7	120	56	67
13	9	8.16	0.070	1.2	120	103	273
14	10	8.06	0.031	4	120	101	199

TABLE 2

Example	Metallocene Component	Molecular Weight		Comonomer Content and Distribution	
		Low Mpk value	High Mpk value	Total Average Comonomer Content SCB/1000C	Comonomer Distribution Low Mpk/high Mpk at mid-position
11	bis-(propenylcyclopentadienyl)ZrC12	40 600	500 000	9	4.2
12	bis-(1,2-propenyl,methylcyclopentadienyl)ZrC12	6 200	612 000	7.4	1.6
13	bis-(1,2-propenyl,methylcyclopentadienyl)ZrC12	5 000	412 000	3.8	1.4
14	bis-(pentamethylcyclopentadienyl)ZrC12	7 500	437 600	5	0.4

Claims

1. A process for preparing bimodal molecular weight distribution copolymers of ethylene with alpha-olefins having 3 to 20 carbon atoms, said copolymers having:-

   (a) a comonomer distribution wherein the comonomer level at the mid-position of the low molecular weight component is <3 times the level at the mid-position of the high molecular weight component, and
   (b) a total average comonomer content in the range 0.5-20 short chain branches (SCB)/1000 C atoms

   wherein said process comprises polymerizing ethylene with alpha olefins in the presence of a supported multisite catalyst, said catalyst comprising a Ziegler catalyst component and a metallocene component having any of the formulae:

$$\text{(I)}\qquad (C_5R_5)(C_5R^1{}_5)MY_2$$

$$\text{(II)}\qquad (C_5R_2H_3)(C_5R^1{}_2H_3)MY_2$$

$$\text{(III)}\qquad (C_5R_4)Z(C_5R^1{}_4)MY_2$$

$$\text{(IV)}\qquad (C_5R_mH_{5-m})(C_5R^1{}_nH_{5-n})MY_2$$

   wherein,

   C_5R_5 and $C_5R^1{}_5$ represent a cyclopentadienyl ligand,
   R and R^1 are alkyl, aryl, alkylaryl, alkenyl, or haloalkyl groups and may be the same or different,
   Z is a bridging group
   M is Zr, Ti or Hf,
   Y is a univalent anionic ligand

   and wherein in Formula (II) at least one of R and R^1 has ≥ 3 carbon atoms and in Formula (IV) m is 3 or 4 and n is 5 or less.

2. A process according to claim 1 wherein the total average comonomer content is in the range 1-20.

3. A process according to claim 1 wherein the multisite catalyst is supported on silica, alumina or magnesium chloride.

4. A process according to claim 1 wherein the bridging group Z is CX_2, SiX_2, or GeX_2 wherein X is hydrogen or a group as defined by R and R^1.

5. A process according to claim 1 wherein Y is a halide or an alkyl or an alkoxy group.

6. A process according to claim 1 wherein the bridging group Z is CX_2, SiX_2, or GeX_2 and Y is a halide or an alkyl or an alkoxy group wherein X is as defined above.

7. A process according to claim 1 wherein M is zirconium.

8. A process according to claim 1 wherein the metallocene component is bis(pentamethylcyclopentadienyl)zirconium dichloride or bis(1-propenyl-2-methylcyclopentadienyl) zirconium dichloride.

9. A process according to claim 1 wherein the multisite catalyst is used in the presence of at least one co-catalyst.

10. A process according to claim 9 wherein the co-catalyst is an organo aluminium compound.

11. A process according to claim 10 wherein the organo aluminium compound is methyl aluminoxane or trimethyl

aluminium.

12. A process according to claim 1 carried out in the gas phase.

Patentansprüche

1. Verfahren zur Herstellung von Copolymeren mit bimodaler Molekulargewichtsverteilung aus Ethylen mit 3 bis 20 Kohlenstoffatome aufweisenden α-Olefinen, wobei die Copolymere aufweisen:

   (a) eine Comonomerverteilung, in der der Comonomeranteil in der mittigen Lage der Komponente mit niederem Molekulargewicht das <3-fache des Anteils in der mittigen Lage der Komponente mit hohem Molekulargewicht beträgt, und
   (b) einen mittleren Comonomergesamtanteil im Bereich von 0,5-20 Kurzkettenverzweigungen (SCB)/1000 C-Atome,

   wobei das Verfahren Polymerisieren von Ethylen mit α-Olefinen in Gegenwart eines getragenen Vielstellen-katalysators umfaßt, wobei der Katalysator eine Ziegler-Katalysatorkomponente und eine Metallocenkomponente mit einer der Formeln:

$$\text{(I)} \qquad (C_5R_5)(C_5R^1{}_5)MY_2$$

$$\text{(II)} \qquad (C_5R_2H_3)(C_5R^1{}_2H_3)MY_2$$

$$\text{(III)} \qquad (C_5R_4)Z(C_5R^1{}_4)MY_2$$

$$\text{(IV)} \qquad (C_5R_mH_{5-m})(C_5R^1{}_nH_{5-n})MY_2$$

   worin

   C_5R_5 und $C_5R^1{}_5$ einen Cyclopentadienylliganden wiedergeben,
   R und R^1 Alkyl-, Aryl-, Alkylaryl-, Alkenyl- oder Halogenalkylgruppen darstellen und gleich oder verschieden sein können,
   Z eine Brückengruppe darstellt,
   M Zr, Ti oder Hf darstellt,
   Y einen einwertigen anionischen Liganden darstellt,

   und wobei in Formel (II) mindestens einer der Reste R und $R^1 \geq 3$ Kohlenstoffatome aufweist und in Formel (IV) m 3 oder 4 ist und n 5 oder weniger ist, umfaßt.

2. Verfahren nach Anspruch 1, wobei der mittlere Comonomergesamtanteil im Bereich 1-20 liegt.

3. Verfahren nach Anspruch 1, wobei der Vielstellenkatalysator auf Siliziumdioxid, Aluminiumoxid oder Magnesium-chlorid getragen wird.

4. Verfahren nach Anspruch 1, wobei die Brückengruppe Z CX_2, SiX_2 oder GeX_2 darstellt, worin X Wasserstoff oder eine wie durch R und R^1 definierte Gruppe bedeutet.

5. Verfahren nach Anspruch 1, wobei Y ein Halogenid oder eine Alkyl- oder eine Alkoxygruppe darstellt.

6. Verfahren nach Anspruch 1, wobei die Brückengruppe Z CX_2, SiX_2 oder GeX_2 darstellt und Y ein Halogenid oder eine Alkyl- oder eine Alkoxygruppe darstellt, wobei X wie vorstehend definiert ist.

7. Verfahren nach Anspruch 1, wobei M Zirconium darstellt.

8. Verfahren nach Anspruch 1, wobei die Metallocenkomponente Bis(pentamethylcyclopentadienyl)zirconiumdichlorid oder Bis (1-propenyl-2-methylcyclopentadienyl)zirconiumdichlorid ist.

9. Verfahren nach Anspruch 1, wobei der Vielstellenkatalysator in Gegenwart von mindestens einem Cokatalysator verwendet wird.

10. Verfahren nach Anspruch 9, wobei der Cokatalysator eine Organo-Aluminium-Verbindung darstellt.

11. Verfahren nach Anspruch 10, wobei die Organo-Aluminium-Verbindung Methylaluminoxan oder Trimethylaluminium darstellt.

12. Verfahren nach Anspruch 1, das in der Gasphase ausgeführt wird.

Revendications

1. Procédé de préparation de copolymères à distribution bimodale du poids moléculaire d'éthylène et d'alpha-oléfines ayant 3 à 20 atomes de carbone, lesdits copolymères ayant :

   (a) une distribution du comonomère dans laquelle la teneur en comonomère à la médiane du composant à bas poids moléculaire est < 3 fois la teneur à la médiane du composant à haut poids moléculaire, et
   (b) la teneur totale moyenne en comonomère est comprise entre 0,5 et 20 ramifications à chaîne courte (SCB)/1000 atomes de C

   dans lequel ledit procédé consiste à polymériser de l'éthylène avec des alpha-oléfines en présence d'un catalyseur multisite sur support, ledit catalyseur comprenant un composant de catalyseur Ziegler et un composant métallocène ayant l'une quelconque des formules :

$$\text{(I)} \quad (C_5R_5)(C_5R^1{}_5)MY_2$$

$$\text{(II)} \quad (C_5R_2H_3)(C_5R^1{}_2H_3)MY_2$$

$$\text{(III)} \quad (C_5R_4)Z(C_5R^1{}_4)MY_2$$

$$\text{(IV)} \quad (C_5R_mH_{5-m})(C_5R^1{}_nH_{5-n})MY_2$$

   dans lesquelles,

   C_5R_5 et $C_5R^1{}_5$ représentent un ligand cyclopentadiényle,
   R et R^1 sont des groupes alkyle, aryle, alkylaryle, alcényle, ou halogénoalkyle et peuvent être identiques ou différents,
   Z est un groupe constituant un pont
   M représente Zr, Ti ou Hf.
   Y est un ligand anionique monovalent

   et dans lesquelles, dans la formule (II), au moins l'un de R et R^1 a ≥ 3 atomes de carbone et, dans la formule (IV), m représente 3 ou 4 et n représente 5 ou moins.

2. Procédé selon la revendication 1 dans lequel la teneur totale moyenne en comonomère est comprise entre 1 et 20.

3. Procédé selon la revendication 1 dans lequel le catalyseur multisite est sur support de silice, d'alumine ou de chlorure de magnésium.

4. Procédé selon la revendication 1 dans lequel le groupe Z constituant un pont représente CX_2, SiX_2, ou GeX_2 dans

lequel X est un atome d'hydrogène ou un groupe défini par R et R^1.

5. Procédé selon la revendication 1 dans lequel Y est un halogénure ou un groupe alkyle ou alkoxy.

6. Procédé selon la revendication 1 dans lequel le groupe Z constituant un pont représente CX_2, SiX_2, ou GeX_2 et Y est un halogénure ou un groupe alkyle ou alkoxy dans lequel X est tel que défini ci-dessus.

7. Procédé selon la revendication 1 dans lequel M est le zirconium.

8. Procédé selon la revendication 1 dans lequel le composant métallocène est le dichlorure de bis(pentaméthylcyclopentadiényl)zirconium ou le dichlorure de bis(1-propényl-2-méthylcyclopentadiényl)zirconium.

9. Procédé selon la revendication 1 dans lequel le catalyseur multisite est utilisé en présence d'au moins un co-catalyseur.

10. Procédé selon la revendication 9 dans lequel le co-catalyseur est un composé d'organo-aluminium.

11. Procédé selon la revendication 10 dans lequel le composé d'organo-aluminium est le méthyl aluminoxane ou le triméthyl aluminium.

12. Procédé selon la revendication 1 effectué en phase gazeuse.